Study of optically active 3-methoxy-*N*-(pyridin-4-yl)pyridin-4-amine intercalated into zirconium 4-sulfophenylphosphonate layers by molecular simulation methods

J. Škoda*, M. Pospíšil, P. Kovář

Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16 Prague 2, Czech Republic
**kuba.skoda@gmail.com*

Keywords: zirconium 4-sulfophenyl phosphonate; 3-methoxy-*N*-(pyridin-4-yl)pyridin-4-amine; molecular simulations; intercalation

Abstract

We used classical molecular simulation methods to study various arrangements of intercalated optically active 4-4’-dipyridylamine derivatives within the interlayers of zirconium 4-sulfophenylphosphonates (**ZrSPhP**). One from these derivatives are the molecules of 3-methoxy-*N*-(pyridin-4-yl)pyridin-4-amine (**moAPY2**), which were placed among the **ZrSPhP** layers. Their mutual positions and orientations were calculated by the molecular simulation methods to find conformations and arrangements with the lowest value of total potential energy and with respect to the values of total dipole moment of the intercalates within the interlayer space. The final calculated model showed partially disordered arrangement of **moAPY2** molecules and higher values of dipole moment compared to the original molecule of *N*-(pyridin-4-yl) pyridin-4-amine (**APY2**) indicating the **moAPY2** molecules to be a promising derivative for non-linear optical applications after solving complications during the chemical synthesis of this type of intercalate.

Introduction

From the point of view of optical applications, materials with non-linear optical properties are of huge interest [1]. Organic push-pull derivatives are one of such molecules [2-4]. Based on the previous calculations, the molecule **moAPY2** (see Fig. 1) – a derivative of the optically active **APY2** molecule – was chosen as a promising derivative for incorporation into the **ZrSPhP** host matrices as a high value of the total dipole moment, a quantity responsible for non-linear properties of this material, was expected. The goal of the intercalation into the matrices is to transfer such useful behaviour into a macroscopic level. Molecular simulations are one of the methods that can be used for determining the arrangement of intercalates and to predict related behaviour of the resultant material which can have promising properties and can be potentially synthesized.

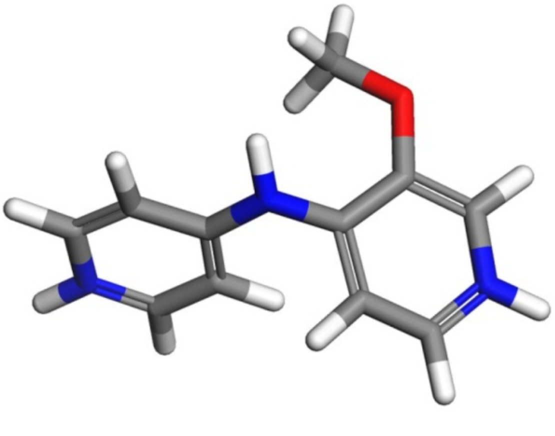

Figure 1. The optimized conformation of the **moAPY2** molecule in the COMPASS force field.

Molecular simulations

The molecular mechanic calculations were performed in the Materials Studio modelling environment [5]. An initial model of the host structure was used from the results of our previous research [6]. The geometry optimization in this case was based on the presumption of the rigidity of the inorganic zirconium-phosphate part of **ZrSPhP** with the -zirconium hydrogen phosphate layered structure determined by Troup and Clearfield [7]. The cell dimension *c* was prolonged so that the interlayer spaces could accommodate the guest molecules. The amount of molecules of the organic derivatives as well as the amount of the water in the interlayer space was taken similarly to the results of chemical analysis of the intercalated molecules of **APY2**. We suppose a protonation of the guest molecules at pyridine nitrogen atoms, like in the case of **APY2**. Thus, two hydrogen atoms were bonded to them and the total charge of the molecule was set to +2 el. The positive charge was compensated by random deletion of hydrogen atoms of the SO_3H groups across the **ZrSPhP** layers which were each set to carry -48 el. The total chemical composition of the calculated models was $Zr_{100}(SPhP)_{200}^{-96}(GUEST)_{48}^{+96}\cdot 150H_2O$. In order to obtain the best potential arrangement of the guest molecules from the point of view of their optical properties, the guest molecules were located in rows in the initial models. Different arrangements were prepared, with two main types of orientations of the guest molecules – the central nitrogen atom facing the same or alternating direction. In the initial models in the Fig. 2, the rows were arranged in two directions – perpendicular or parallel to cell axis *a* – or in their combination for two adjacent interlayers.

All geometry optimizations were performed using the COMPASS force-field [8]. Charges were adjusted using the Qeq method [9], the electrostatic interactions were calculated using the Ewald summation [10-11], van der Waals energy was evaluated with Lennard-Jones potential with a cut-off of 12 Å. The quench molecular dynamics was done in an NVT statistical ensemble preserving the number of particles, the volume and the temperature of the system. Berendsen thermostat [12] was set to 300 K. Dynamics was calculated with the time-step of 1 fs with 10^6 steps. During the simulations, the **ZrSPhP** atomic positions were kept fixed except of the sulfonate groups.

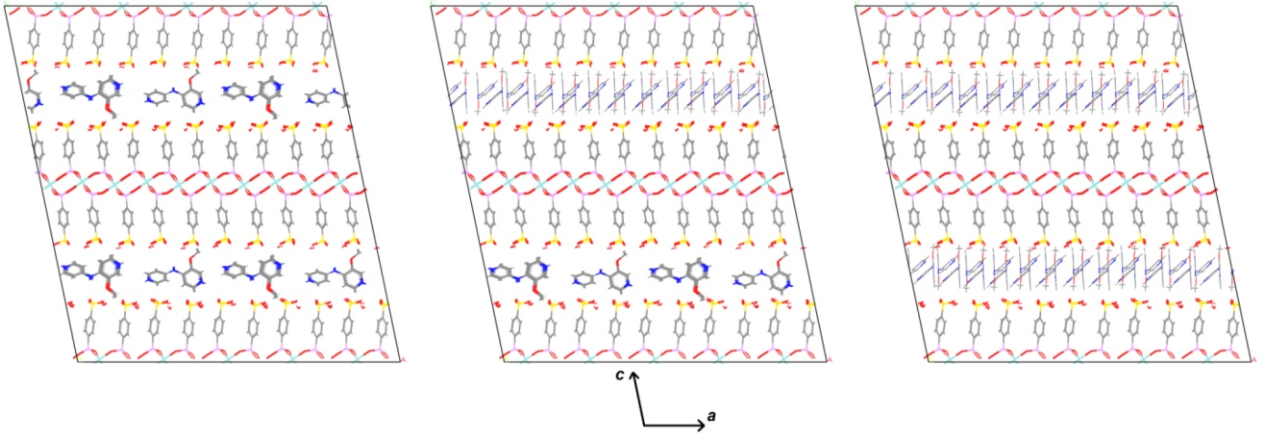

Figure 2. Different initial orientations of **moAPY2** molecules related to *a*-axis.

Results

The results of the geometry optimizations showed us possible arrangements of the concerned molecules within the interlayer space of **ZrSPhP** which allowed us to better understand and predict the resultant properties of the real intercalate. Due to the fact that the material with intercalated molecules of **moAPY2** has not yet been successfully synthesized experimentally, it is not possible to compare the experimental data with the calculated ones as it is done conventionally, for example using the X-ray diffraction. Moreover the amount of the intercalated molecules is not verified experimentally. For those purposes, the information about intercalation of original molecule of **APY2,** simulated in our previous research [13] and after cell refinement [14], was used as fundamental data for the **moAPY2** derivative. This study is therefore focused only on the comparison of different arrangements with respect to the total value of potential energy and on the comparison of their dipole moments which is the important value for optical application purposes.

The presented structure is the model with the lowest potential energy – see Fig. 3. The simulations revealed that the alternating orientation of the intercalated molecules is preferred. One can see a disordered arrangement of the **moAPY2** molecules. At several places, the intercalated molecules even trench into the sulfo- groups' region. It is apparent that in this case the rows were initially arranged in the perpendicular directions to each other. As this is the most probable model, we can say that there is not one preferred direction of the rows. From the top of view, see Fig. 4, it is evident that the intercalated molecules only partially hold their initial row arrangement. It is possible to see that the molecules are kept together in this arrangement by the interactions of the pyridine rings. Water molecules are mostly located in the thin sheets between the **moAPY2**

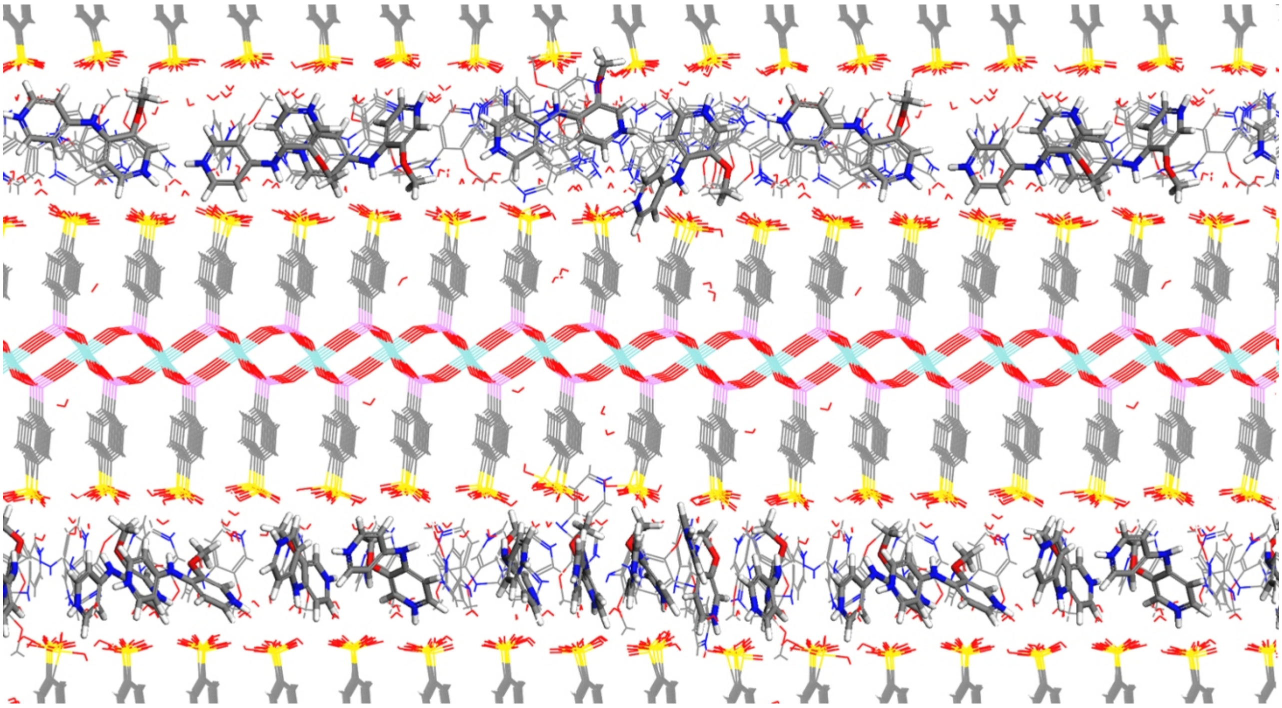

Figure 3. The optimized arrangement of the intercalated **ZrSPhP** with **moAPY2** molecules, a side view.

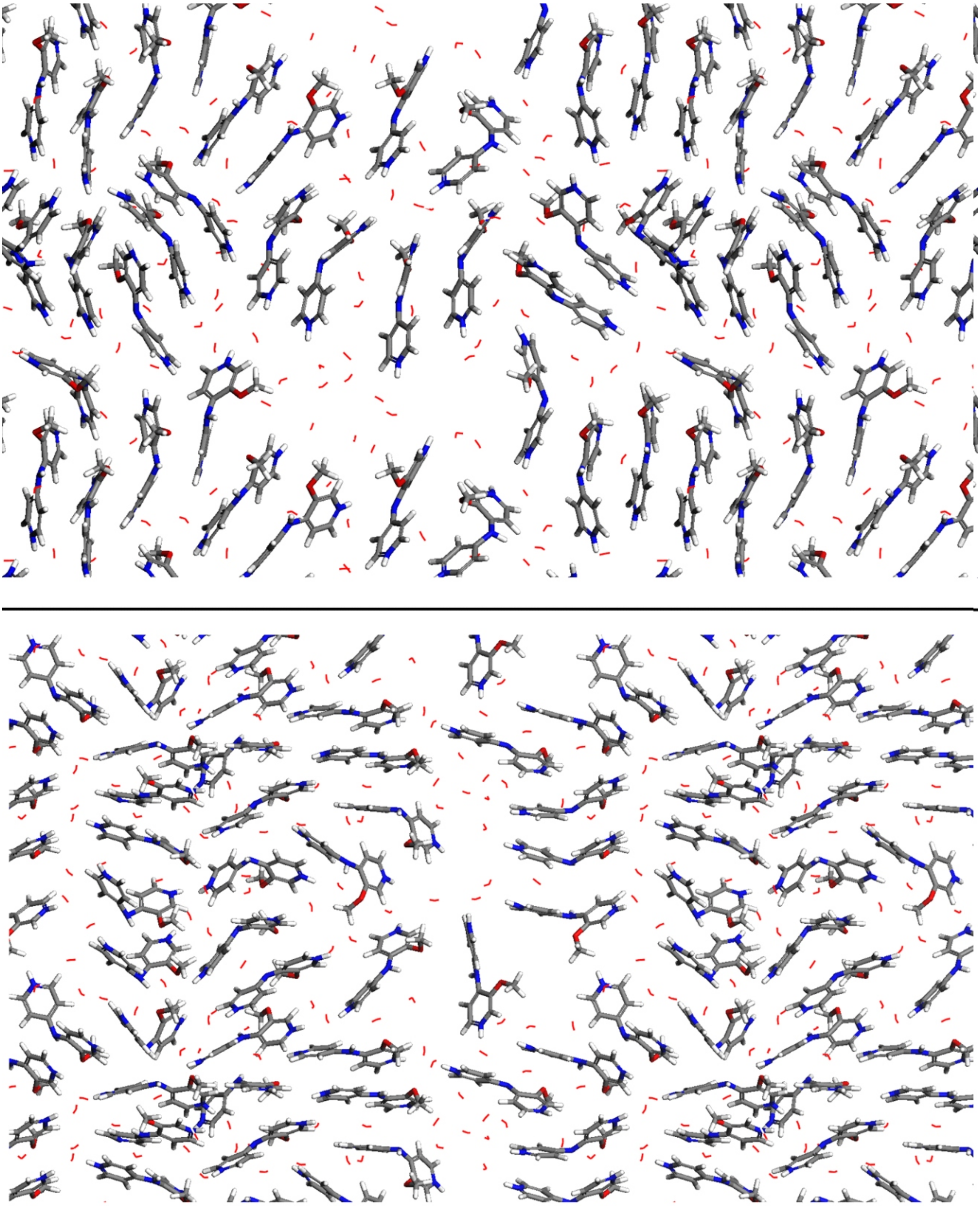

Figure 4. Disordered arrangement of the **moAPY2** intercalate between the layers of **ZrSPhP**, a top view on two interlayer spaces.

molecules and SO_3^- groups of the **ZrSPhP**, see the concentration profile in the Fig. 5. Wide distribution of the positions of **moAPY2**'s nitrogen atoms confirms disordered arrangement of the guests.

In order to better understand the characteristics of the intercalated **ZrSPhP** for its potential use as non-linear optics material, we calculated dipole moments of **APY2** and its **moAPY2** derivative for comparison. The total dipole moments and their components were calculated for all molecules within one interlayer. In the case of **APY2**, we calculated the dipole moment vector ***D*** of the guests for the arrangement with alternating positions of central NH for a direct comparison. The results are summarized in the Table 1. Dipole moment is influenced by the disorder of the guests' arrangement in the interlayer space. The size of the ***D*** vector of the guests in **ZrSPhP** models containing **moAPY2** is much larger than in the case of **APY2** molecules and the size of ***D*** vector of the guests indicates that

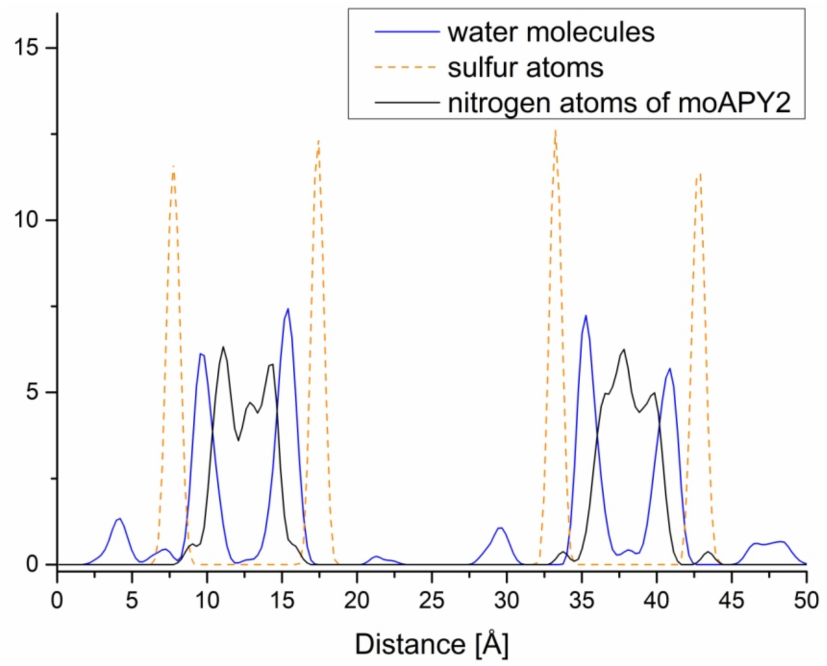

Figure 5. Concentration profile of **ZrSPhP** interlayers with the distribution of water molecules, sulfur atoms and all nitrogen atoms in **moAPY2** along *c* cell coordinate.

Table 1. Comparison of the dipole moments [Debye] for the molecules of **APY2** and **moAPY2** intercalated into **ZrSPhP**.

Dipole moment [D]	D_x	D_y	D_z	$\|D\|$
APY2 [13]	-1.3	-4.0	-4.7	6.3
moAPY2	-104.0	-17.5	22.4	107.8

ZrSPhP-moAPY2 could be, based on the calculation, a good candidate for the non-linear optics applications.

Conclusion

The calculated structure of **ZrSPhP** with **moAPY2** molecules in the interlayer space was built and optimized in the Materials Studio software package. The most probable model with the minimum energy showed us preferred irregular distribution of the optically active **moAPY2** molecules with partial row arrangement. Water molecules are mostly located in the sheets between the **moAPY2** molecules and the SO_3^- groups. Different orientations of the intercalated molecules have an impact on the total dipole moment of the material which plays a key role in the potential optical applications.

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Jakub Škoda thanks to project SVV260586 "Studentský výzkum v oboru biofyzika a chemická fyzika" for financial support.